
(12) UK Patent Application (19) GB (11) 2 073 224 A

(21) Application No 8109281

(22) Date of filing 25 Mar 1981

(30) Priority data

(31) 20888

(32) 25 Mar 1980

(33) Italy (IT)

(43) Application published
14 Oct 1981

(51) INT CL³
C08G 69/48 59/14 69/34

(52) Domestic classification

C3R 22D1A2 22D1A3

22D1AX 22D1B2 22D1BX

22D2A1 22N1A 22N1B

22T2 J

C3B 1D2C 1N1G F

C3K 201 GX

C3M 105C 106C 116C

155 A

C3Y B262 B263 B270

F230 F581

(56) Documents cited

GB 631020

GB 616443

GB 610311

GB 610304

GB 507244

(58) Field of search

C3R

(71) Applicants

Chem-Plast S.p.A., Piazza

Vetra 21, Milan, Italy

(72) Inventor

Italo Albini

(74) Agents

Abel & Imray,

Northumberland House,

303—306 High Holborn,

London WC1V 7LH

(54) Amino-polyamides and derivatives thereof useful as plastisol adhesion improvers

(57) 1 to 2 equivalents of polyamines $H_2N(CH_2)_x - (NH(CH_2)_g)_n - NH_2$, wherein x, g and n are each independently at least 2, are homo- or co-polymerised with (a) 1 to 0.5 equivalents of dicarboxylic acids and (b) 0 to 0.5 equivalents of polymeric fat acids. They may be reacted with epoxy resins or converted to

ketamines by treatment with ketones.

The adhesion of plastics to adhesion-rejecting surfaces can be improved by adding to plastics, e.g. of PVC, compounds the above polyamides or reaction products which afford a high content of amine groups, amide bridges as such or as imidazoline rings in comparatively small concentrations relative to the plastics concerned so as to improve adhesion while leaving the other physical properties of the plastics unaltered.

GB 2 073 224 A

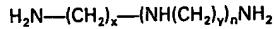
SPECIFICATION
Plastisol adhesion improvers

It is known that the plastiols are essentially comprised of a liquid dispersion of a powdered polymer in a plasticizer in which the polymer must not be appreciably soluble at room temperature.

5 When the plastiols are subjected to the action of heat, a dissolution of the polymer in the plasticizer is experienced with the attendant formation of a more or less elastic homogeneous mass.

The plastiols are mainly used as heat-insulating and noise-insulating layers, for example in the automotive industry, by applications onto metal surfaces of different kinds, the adhesion properties of which are, however, very poor. It is known long since that, according to the common experience, such 10 adhesion is improved if plastiols are supplemented by polyamide resins capable of being homogeneously dispersed therethrough. According to the known art, the most adapted to the purpose have proven to be the polyaminoimide and polyamineamido imidazoline resins prepared by condensation of aliphatic polyamines with polycarboxylic acids as obtained by polymerization of unsaturated fatty acids, the adducts with epoxy resins obtained thereby and the ketoimines which can 15 be prepared by treating said resins with ketones.

The aliphatic polyamines referred to above have the general formula:

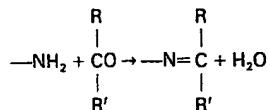


wherein x, y and n are integers, equal to or different from one another and higher than 2.

Said polycarboxylic acids, as obtained by polymerization of unsaturated fatty acids, are composed 20 by mixture of polymers of unsaturated fatty acids having 18 carbon atoms, having a composition lying in the following ranges: 0% to 2% of monomers, 58% to 98% of dimers and 2% to 40% of trimers.

The epoxy adducts deriving from the resins aforementioned are obtained by reacting such resins with the products containing end epoxy groups, such as the polyglycidyl ethers of polyhydroxyl phenols.

The ketoimines are obtained by treating the above indicated resins with ketones, so as to convert 25 the primary amine groups into ketoimine groups with water withdrawal, according to the following reaction pattern:



It has been experimentally ascertained, however, that with the polyaminoamide and the polyaminoamidoimidazoline resins which are known and of the kind referred to above, and with the 30 adducts and the ketoimines obtained thereby, poor results because, while the adhesive force of plastisol is increased as the quantity of the added resin is increased, such a quantity cannot exceed, in practice, a certain level beyond which certain properties of the plastisol, such as applicability and cohesion of the end coating product would be altered. In addition it should be considered that the use of such resins in high amounts would be economically objectionable.

35 The property of exaltation of the adhesion of plastisol by polyaminoamide resins and polyaminoamidoimidazoline resins and their adducts with epoxy resins has been discovered by trial and error by testing a number of different products.

This invention has matured from the theoretical consideration that, in actual practice, the adhesive 40 properties of the resins are a function of their content of amine groups and amide bridges, as such and converted into imidazoline rings, such as in the case of the polyaminoamidoimidazoline resins and that consequently the activity of such compounds as adhesion-promoters for such resins is a specific 45 function of their content of amine groups, amide bridges and imidazoline bridges. On this basis, the present invention thus aims at preparing polyaminoamide resins, or polyaminoamidoimidazoline resins, characterized by a high number of amine groups and amide bridges, as such or in the form of imidazoline bridges, which are dispersable in the plastiols, thereby imparting thereto high adhesion 50 properties even if such promoters are present in low concentrations.

By virtue of such an idea one would solve the problem of using the resins of the kind referred to above, even though, in general, such resins should be used in great amounts to achieve satisfactory results as to the improvements of adhesion, but, as outlined above, such high amounts of resins would 55 impair other basic properties of the plastiols irremediably.

To achieve this object, the present invention suggests polyaminoamide and polyaminoamidoimidazoline resins principally suitable for use as plastisol adhesion promoters, characterized by a high content of amide groups, amide bridges as such or in the form of imidazoline rings, as obtained by condensing:

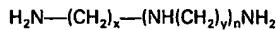
55 a) from 0 to 0.5 equivalents of polycarboxylic acids deriving from the polymerization of unsaturated fatty acids having a composition lying within the following ranges: 0% to 2% of monomers;

58% to 98% of dimers and 2% to 40% of trimers, and

b) from 0.5 to 1 equivalent of aliphatic, saturated or unsaturated dicarboxylic acids, having a straight or a branched chain of not more than 12 carbon atoms and/or saturated and unsaturated dicarboxylic cycloaliphatic acids and/or aromatic dicarboxylic acids with:

5 — from 1 to 2 equivalents of aliphatic polyamines having the general formula:

5



wherein x, y and n are integers, equal to or different from one another, and higher than 2.

The resins according to this invention are thus characterized in that they are condensation derivatives of dicarboxylic acids. If these acids are in admixture with fatty acids which have been 10 polymerized according to point a) as defined hereinbefore, such dicarboxylic acids are present in the admixture in an amount equal to at least the 50% of equivalents of such fatty acids.

10

Those dicarboxylic acids can be: aliphatic, with a straight or branched, saturated or unsaturated chain, having not more than 12 carbon atoms, such as oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, trimethyladipic, maleic and fumaric acids; or they can be saturated or 15 unsaturated dicarboxylic acids, such as hexahydrophthalic, tetrahydrophthalic acids, or aromatic dicarboxylic acids such as phthalic, isophthalic and terephthalic acids.

15

The invention also relates to epoxy adducts, as obtained by treating with epoxy resins such as the diglycidyl ether of the p,p'-isopropylidenebiphenol, said polyaminoamide or polyaminoamidoimidazoline resins. The invention also encompasses the corresponding ketoimines as obtained by treating said 20 resins with ketones such as methylethylketone.

20

Resins, and their adducts and ketoimine derivatives, according to this invention, can be employed as adhesion promoters for plastisols, both as such and in solution. Both the concentration of the solution and the type of the solvent used can be varied consistently with the viscosity of the resins and its solubility.

25

25 The solvents which are adapted to this purpose can be selected from among a wide range of organic compounds, such as hydrocarbons, their chlorinated or nitrous derivatives, alcohols, polyols, esters, ketones, amines and amides. A preferred solvent is benzyl alcohol.

In order that the resins according to the invention may be more comprehensively described, a few 30 examples of preparation thereof are reported hereinafter, these examples being numbered from 6 to 12, which are given by way of illustration only.

30

Before these examples from 6 to 12, the examples numbered from 1 to 5 are concerned with the preparation of resins according to the conventional art so that examples from 1 to 5 hereof must be intended as merely comparative examples to permit a comparison with the resins the subject of this invention, as will be expounded in more detail hereinafter.

35 EXAMPLE 1 (COMPARATIVE EXAMPLE)

35

A polyaminoamide resin from polymerized fatty acids. —

285 parts by weight (1 equivalent) of polymerized fatty acids (obtained from unsaturated fatty acids having 18 carbon atoms and having the following composition: 1% of monomers, 77% of dimers and 22% of trimers, by wt) are heated with stirring with 131.4 parts by wt (1.8 equivalents) of 40 triethylenetetramine, until reaching a temperature of 220°C and they are maintained at such a temperature until 18 parts by weight of water are dispelled, whereafter heating is discontinued. The resin thus obtained is dissolved in 170 parts by weight of benzyl alcohol in order to lower the viscosity and rendering the resin readily and homogeneously dispersible in the plastisol.

40

45 EXAMPLE 2 (COMPARATIVE EXAMPLE)

45

An epoxy adduct of a polyaminoamide resin from polymerized fatty acids. —

100 parts by weight of the solution obtained according to the procedure of Example 1 hereof are supplemented with 3.5 parts by weight of the diglycidyl ether of the p,p'-isopropylidenebiphenol and 1.5 parts by wt of benzyl alcohol. Thereafter, the mass is maintained for at least one hour at a temperature of about 100°C.

50 EXAMPLE 3 (COMPARATIVE EXAMPLE)

50

A ketoimine of a polyaminoamide resin from polymerized fatty acids. —

A polyaminoamide resin is prepared with the same raw materials, quantities and conditions as in Example 1 hereof. Prior to proceeding with the dissolution in benzyl alcohol, there are added 288 parts by wt (4 mol) of methylethylketone and 74 parts by wt of cyclohexane (water-entrainer). The mass is 55 brought to a boil and the distillate recirculated so as to separate water as it is being formed. The operation is continued until the formation of water is over, whereafter the excess of methylethylketone and the cyclohexane are distilled off. The product is then dissolved in 187 parts by wt of benzyl alcohol.

55

EXAMPLE 4 (COMPARATIVE EXAMPLE)*A polyaminoamidoimidazoline resin from polymerized fatty acids. —*

285 parts by wt (1 equivalent) of polymerized fatty acids (such as described in Example 1 hereof) are heated, with stirring, with 131.4 parts by wt (1.8 equivalent) of triethylenetetramine, until attaining 5 a temperature of 260°C and such a temperature is maintained until 27 parts of water, by wt, are eliminated: thereafter heating is discontinued. The resin thus obtained is dissolved in 165 parts by wt of benzyl alcohol.

5

EXAMPLE 5 (COMPARATIVE EXAMPLE)*An epoxy adduct of a polyaminoamidoimidazoline resin. —*

10 The solution as obtained according to the procedure of Example 4 hereof is treated in the same 10 way as disclosed in Example 2 hereof.

EXAMPLE 6 (INVENTION)*A polyaminoamide resin from polymerized fatty acids and an aliphatic dicarboxylic acid. —*

15 85.5 parts by wt (0.3 equivalent) of polymerized fatty acids (such as described in Example 1 hereof) and 51.1 parts by wt (0.7 equivalent) of adipic acid with 131.4 parts by wt (1.8 equivalent) of 15 triethylenetetramine are treated in the manner described in Example 1 hereof. The resin thus obtained is dissolved in 107 parts by wt of benzyl alcohol.

EXAMPLE 7 (INVENTION)*An epoxy adduct of a polyaminoamide resin from polymerized fatty acids and an aliphatic*

20 *bicarboxylic acid. —* The solution as obtained according to what has been disclosed in Example 6 hereof, is treated in the same way as described in Example 2 hereof.

20

EXAMPLE 8 (INVENTION)*A ketoinime of a polyaminoamide resin from polymerized fatty acids and a dicarboxylic aliphatic*

25 *acid. —* A polyaminoamide resin is prepared with the same raw materials, quantities and conditions as suggested in Example 6 hereof. Prior to proceeding with the dissolution in benzyl alcohol, the ketoimination procedure of Example 3 hereof is proceeded with, whereafter the resultant product is dissolved in 123 parts by wt of benzyl alcohol.

25

30 **EXAMPLE 9 (INVENTION)** *A polyaminoamidoimidazoline resin from polymerized fatty acids and an aliphatic dicarboxylic*

acid. —

35 The same amounts of substances as listed in Example 6 hereof are treated according to the procedure as described in Example 4 hereof. The resin thus obtained is dissolved in 99 parts by wt of 35 benzyl alcohol.

30

35

EXAMPLE 10 (INVENTION)*An epoxy adduct of a polyaminoamidoimidazoline resin from polymerized fatty acids and an**aliphatic dicarboxylic acid. —*

40 The solution as obtained according to Example 9 hereof is treated in the same way as disclosed in 40 Example 2 hereof.

40

EXAMPLE 11 (INVENTION)*A polyaminoamide resin from polymerized fatty acids and an aromatic dicarboxylic acid. —*

45 85.5 parts by wt (0.3 equivalent) of polymerized fatty acids (as described in Example 1 hereof) and 58.1 parts by wt (0.7 equivalent) of isophthalic acid, with 131.4 parts by wt (1.8 equivalent) of triethylenetetramine are treated in the same way as described in Example 1 hereof. The resin thus obtained is dissolved in 110 parts by wt of benzyl alcohol.

45

EXAMPLE 12 (INVENTION)*An epoxy adduct of a polyaminoamide resin from polymerized fatty acids and an aromatic*

50 *bicarboxylic acid. —* The solution as obtained according to what has been disclosed in Example 9 is treated in the same 50 way as described in Example 2 hereof.

All the products of the Examples hereof are comprised of solutions of resins or adducts at 70% concentration in benzyl alcohol, the latter acting both as a solvent and a dispersing agent.

55 Comparative tests have been carried out in order to evaluate the magnitude of the adhesion promotion of the resins with respect to plastisols (adhesion-promoting action); the resins have been prepared according to the Examples set forth hereinbefore.

55

All tests have been conducted on a plastisol having the following percentage composition, on a weight basis:

	Polyvinyl chloride	33%	
	Diethyl phthalate	34%	
5	Titanium dioxide	8%	5
	Kaolin	10%	
	Colloidal silica	0.5%	
	Diglycidyl ether of 1,4-butanediol	0.4%	
	An adhesion promoter	1%	

10 The tests have been conducted by subjecting to the tensile shear stress test two steel slabs having 10 the size of 100 by 25 mm roughened with emery cloth and glued with a layer of the plastisol being tested having a thickness of 2 mm the surface being 250 mm², the plastiols having been cured at 140°C for 30 mins.

15 The results obtained with the products which had been prepared in the Examples hereof from 1 to 15 12, are tabulated in the attached Table.

TABLE

Adhesion-Promoter	Average Tensile Shear Stress (Average of 5 tests) Kg/cm ²
Example No. 1	3.6
Example No. 2	4.1
Example No. 3	7.5
Example No. 4	4.6
Example No. 5	4.8
Example No. 6	17.5
Example No. 7	18.1
Example No. 8	28.2
Example No. 9	18.9
Example No. 10	19.5
Example No. 11	17.3
Example No. 12	17.9

The above tabulated data show that the products according to the invention, that is the adhesion-promoters of the Examples from 6 to 12 inclusive hereof impart to the plastisol a tensile shear stress resistance which is considerably improved over that which is experienced with the products according 20 to the conventional art (that is, those of Examples hereof from 1 to 5 inclusive), the dosages of adhesion-promoter relative to the plastisol being the same for all the Examples indiscriminately.

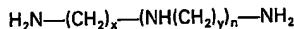
The facts set forth above show that the resins made according to the invention, as well as their 25 epoxy and ketoimine derivatives, are capable of improving to a degree the adhesion of the plastiols to the metallic surfaces, even in low concentrations, at which no hazard exists of jeopardizing the other properties of the plastiols, such as applicability and cohesion of the final coatings.

CLAIMS

1. Polyaminoamide resins and polyaminoamidoimidazoline resins characterized in that they are obtained by condensing:

5 a) from 0 to 0.5 equivalent of polycarboxylic acids derived from the polymerization of unsaturated fatty acids having a composition lying within the following ranges: 0 to 2% of monomers, 58% to 98% of dimers and 2% to 40% of trimers, and

5 b) from 0.5 to 1 equivalent of bicarboxylic acids, with from 1 to 2 equivalents of aliphatic polyamines having the general formula:



10 wherein x, y and n are integers, equal to or different from one another and higher than 2. 10

11 2. Resins according to Claim 1, characterized in that said bicarboxylic acids are aliphatic acids, saturated or unsaturated, with a straight or a branched chain of not more than 12 carbon atoms.

12 3. Resins according to Claim 1, characterized in that said bicarboxylic acids are cycloaliphatic, saturated or unsaturated acids.

15 4. Resins according to Claim 1, characterized in that said bicarboxylic acids are aromatic acids. 15

16 5. Resins according to Claim 2, characterized in that said aliphatic bicarboxylic acids are members selected from the group consisting of: adipic, oxalic, malonic, succinic, glutaric, pimelic, suberic, azelaic, sebatic, trimethyladipic, maleic and fumaric acids.

17 6. Resins according to Claim 3, characterized in that said cycloaliphatic bicarboxylic acids are members selected from the group consisting of: hexahydrophthalic and tetrahydrophthalic acids. 20

18 7. Resins according to Claim 4, characterized in that said aromatic bicarboxylic acids are members selected from the group consisting of: phthalic, isophthalic and tetraphthalic acids.

19 8. Epoxy adducts as obtained by treating with epoxy resins any of the polyaminoamide and polyaminoamidoimidazoline resins as claimed in Claim 1.

25 9. Adducts according to Claim 8, characterized in that said epoxy resin is the diglycidyl ether of the 25 p,p'-isopropylidenebiphenol.

26 10. Ketoimines as obtained by treating with ketones any of the polyaminoamide and polyaminoamidoimidazoline resins as claimed in Claim 1.

27 11. Ketoimines according to Claim 10, characterized in that said ketone is methylethylketone.

30 12. Polyaminoamide resins and polyaminoamidoimidazoline resins, their epoxy adducts and ketoimines according to the preceding Claims, characterized in that they are dissolved in an organic solvent. 30

31 13. Resins, epoxy adducts and ketoimines according to Claim 12, characterized in that they are dissolved in a concentration comprised between 10% and 95% on a weight basis.

35 14. Resins, epoxy adducts and ketoimines according to Claim 12, characterized in that said solvent is benzyl alcohol. 35

36 15. Resins, epoxy adducts and ketoimines substantially as hereinbefore described with reference to the Examples from 6 to 12 hereof.

37 16. Adhesion-promoters for plastiols characterized in that they consist of a polyaminoamide or a polyaminoamidoimidazoline resin or any of their epoxy adducts or a corresponding ketoimine as claimed 40 in any of the preceding Claims.

38 17. Plastiols characterized in that they contain as an adhesion-promoter a resin or an epoxy adduct thereof or a corresponding ketoimine as claimed in any of the preceding Claims.

40 18. A process for preparing the products according to the preceding Claims, substantially as 40 described in the Examples attached to the specification. 45